Supplementary Material for Chemical Communications

Supplementary Information

Intramolecular Charge-Transfer Fluorescence of 1-Phenyltridecamethylbicyclo[2.2.2]octasilane

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1. X-ray Structural analysis of 1-phenylbicyclo[2.2.2]octasilane (1)

Table S1. Crystal data and structure refinement for 1-phenylbicyclo[2.2.2]octasilane (**1**).

Identification code	PhBCOS	
Empirical formula	C_{19} H_{44} Si_8	
Formula weight	497.26	
Temperature	173(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/n$	
Unit cell dimensions	a = 9.9526(5) Å	α = 90°.
	b = 16.4089(9) Å	β = 92.026(3)°.
	c = 18.5655(11) Å	γ = 90°.
Volume	3030.1(3) Å^3	
Z	4	
Density (calculated)	1.090 Mg/m^3	
Absorption coefficient	0.360 mm^{-1}	
F(000)	1080	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	3.20 to 27.48°.	
Index ranges	0<=h<=12, 0<=k<=21, -24<=l<=24	
Reflections collected	6868	
Independent reflections	6868 [R(int) = 0.0000]	
Completeness to theta = 27.48°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9649 and 0.8997	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6868 / 0 / 244	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.1082	
R indices (all data)	R1 = 0.0607, wR2 = 0.1168	
Largest diff. peak and hole	0.885 and -0.421 e.Å^{-3}	

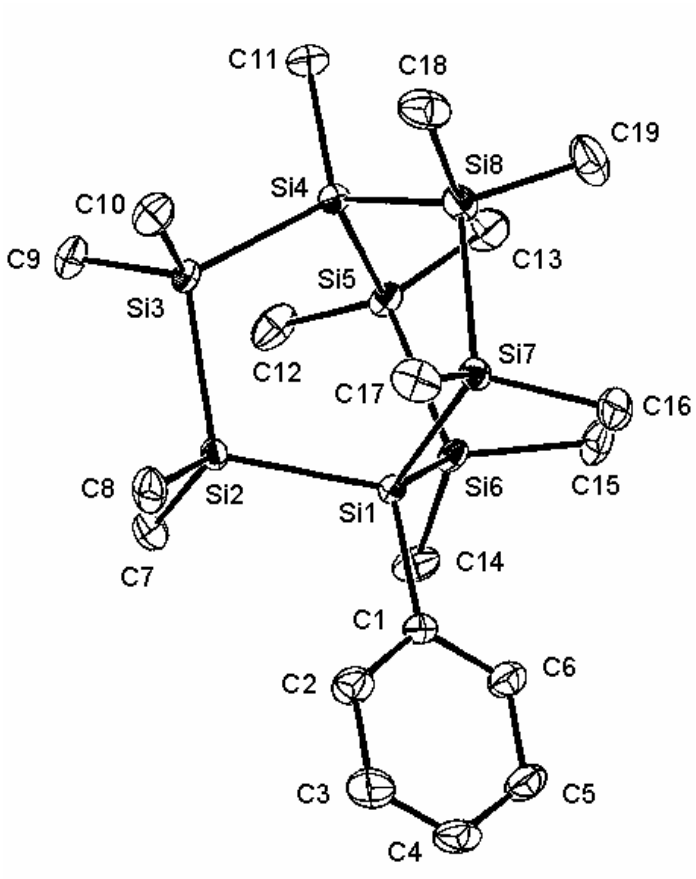

Figure S1. ORTEP drawing of 1-phenylbicyclo[2.2.2]octasilane. Hydrogen atoms are omitted for clarity. (30% thermal ellipsoide)

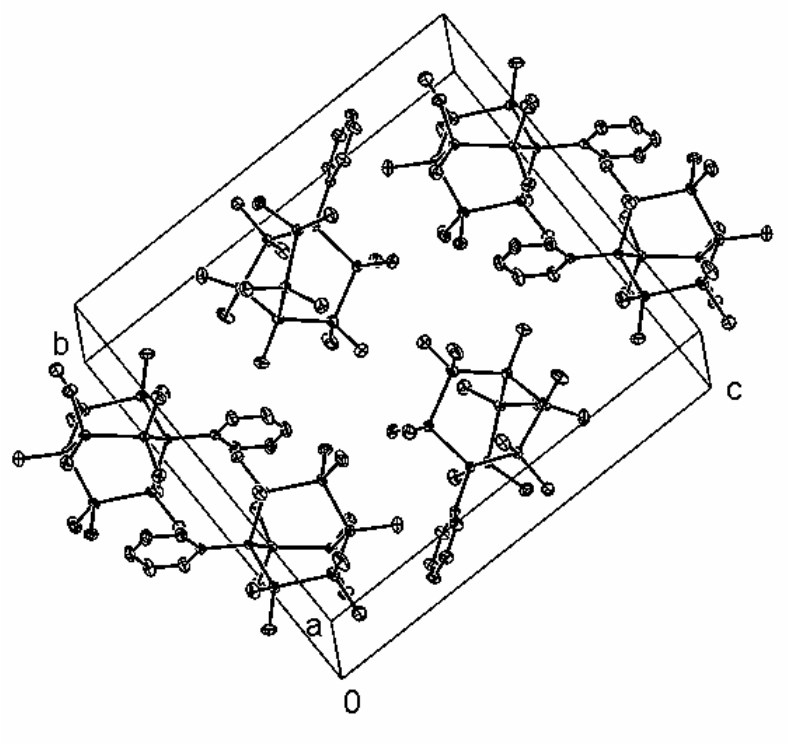

Figure S2. Packing of 1-phenylbicyclo[2.2.2]octasilane.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1-phenylbicyclo[2.2.2]octasilane (**1**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	8030(1)	1889(1)	4855(1)	22(1)
Si(2)	10255(1)	1992(1)	5325(1)	27(1)
Si(3)	10333(1)	2912(1)	6302(1)	28(1)
Si(4)	8165(1)	3140(1)	6707(1)	29(1)
Si(5)	7186(1)	1860(1)	6871(1)	31(1)
Si(6)	6707(1)	1281(1)	5736(1)	28(1)
Si(7)	7186(1)	3202(1)	4647(1)	30(1)
Si(8)	6980(1)	3873(1)	5782(1)	39(1)
C(1)	7937(2)	1255(1)	3994(1)	28(1)
C(2)	9039(3)	1172(2)	3564(1)	49(1)
C(3)	9003(3)	692(2)	2948(2)	61(1)
C(4)	7854(3)	284(2)	2751(1)	54(1)
C(5)	6742(3)	350(2)	3166(1)	51(1)
C(6)	6785(3)	832(2)	3782(1)	43(1)
C(7)	10821(3)	953(1)	5639(2)	44(1)
C(8)	11499(2)	2368(2)	4650(1)	47(1)
C(9)	11499(3)	2504(2)	7039(1)	46(1)
C(10)	11075(3)	3903(2)	5993(2)	49(1)
C(11)	8213(3)	3736(2)	7583(1)	48(1)
C(12)	8365(3)	1167(2)	7406(1)	50(1)
C(13)	5590(3)	1951(2)	7389(2)	59(1)
C(14)	7011(3)	151(1)	5773(1)	45(1)
C(15)	4854(2)	1463(2)	5530(1)	48(1)
C(16)	5503(3)	3163(2)	4153(1)	51(1)
C(17)	8351(3)	3788(2)	4059(2)	52(1)
C(18)	7659(4)	4944(2)	5733(2)	61(1)
C(19)	5137(3)	3974(2)	5976(2)	67(1)

Table S3. Bond lengths [Å] and angles [°] for 1-phenylbicyclo[2.2.2]octasilane (**1**).

Si(1)-C(1)	1.906(2)	C(10)-Si(3)-Si(4)	109.63(9)
Si(1)-Si(7)	2.3404(8)	C(9)-Si(3)-Si(4)	112.01(9)
Si(1)-Si(6)	2.3568(8)	C(10)-Si(3)-Si(2)	108.68(9)
Si(1)-Si(2)	2.3573(8)	C(9)-Si(3)-Si(2)	109.49(9)
Si(2)-C(7)	1.882(2)	Si(4)-Si(3)-Si(2)	110.12(3)
Si(2)-C(8)	1.895(2)	C(11)-Si(4)-Si(5)	110.42(9)
Si(2)-Si(3)	2.3591(8)	C(11)-Si(4)-Si(3)	111.25(9)
Si(3)-C(10)	1.884(2)	Si(5)-Si(4)-Si(3)	106.90(3)
Si(3)-C(9)	1.886(2)	C(11)-Si(4)-Si(8)	110.87(9)
Si(3)-Si(4)	2.3402(8)	Si(5)-Si(4)-Si(8)	110.50(3)
Si(4)-C(11)	1.897(2)	Si(3)-Si(4)-Si(8)	106.77(3)
Si(4)-Si(5)	2.3395(8)	C(12)-Si(5)-C(13)	107.27(14)
Si(4)-Si(8)	2.3753(9)	C(12)-Si(5)-Si(4)	110.81(8)
Si(5)-C(12)	1.891(3)	C(13)-Si(5)-Si(4)	110.88(10)
Si(5)-C(13)	1.892(3)	C(12)-Si(5)-Si(6)	109.32(9)
Si(5)-Si(6)	2.3442(8)	C(13)-Si(5)-Si(6)	109.91(9)
Si(6)-C(14)	1.880(2)	Si(4)-Si(5)-Si(6)	108.63(3)
Si(6)-C(15)	1.894(2)	C(14)-Si(6)-C(15)	108.49(13)
Si(7)-C(16)	1.882(3)	C(14)-Si(6)-Si(5)	109.90(8)
Si(7)-C(17)	1.883(3)	C(15)-Si(6)-Si(5)	106.47(9)
Si(7)-Si(8)	2.3930(9)	C(14)-Si(6)-Si(1)	110.43(9)
Si(8)-C(18)	1.887(3)	C(15)-Si(6)-Si(1)	110.88(9)
Si(8)-C(19)	1.888(3)	Si(5)-Si(6)-Si(1)	110.57(3)
C(1)-C(6)	1.386(3)	C(16)-Si(7)-C(17)	106.91(13)
C(1)-C(2)	1.386(3)	C(16)-Si(7)-Si(1)	110.94(9)
C(2)-C(3)	1.388(4)	C(17)-Si(7)-Si(1)	109.97(9)
C(3)-C(4)	1.364(4)	C(16)-Si(7)-Si(8)	109.99(9)
C(4)-C(5)	1.375(4)	C(17)-Si(7)-Si(8)	110.40(9)
C(5)-C(6)	1.391(3)	Si(1)-Si(7)-Si(8)	108.63(3)
		C(18)-Si(8)-C(19)	106.20(16)
C(1)-Si(1)-Si(7)	110.93(6)	C(18)-Si(8)-Si(4)	109.68(10)
C(1)-Si(1)-Si(6)	109.87(7)	C(19)-Si(8)-Si(4)	111.55(10)
Si(7)-Si(1)-Si(6)	107.36(3)	C(18)-Si(8)-Si(7)	110.15(10)
C(1)-Si(1)-Si(2)	111.48(7)	C(19)-Si(8)-Si(7)	108.81(10)
Si(7)-Si(1)-Si(2)	108.76(3)	Si(4)-Si(8)-Si(7)	110.37(3)
Si(6)-Si(1)-Si(2)	108.32(3)	C(6)-C(1)-C(2)	116.8(2)
C(7)-Si(2)-C(8)	107.70(12)	C(6)-C(1)-Si(1)	121.74(17)
C(7)-Si(2)-Si(1)	108.45(8)	C(2)-C(1)-Si(1)	121.42(17)
C(8)-Si(2)-Si(1)	114.00(8)	C(1)-C(2)-C(3)	122.2(3)
C(7)-Si(2)-Si(3)	109.84(9)	C(4)-C(3)-C(2)	119.8(3)
C(8)-Si(2)-Si(3)	107.20(9)	C(3)-C(4)-C(5)	119.6(2)
Si(1)-Si(2)-Si(3)	109.59(3)	C(4)-C(5)-C(6)	120.3(3)
C(10)-Si(3)-C(9)	106.81(12)	C(1)-C(6)-C(5)	121.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1-phenylbicyclo[2.2.2]octasilane (**1**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	22(1)	24(1)	21(1)	0(1)	1(1)	-2(1)
Si(2)	20(1)	31(1)	29(1)	0(1)	2(1)	1(1)
Si(3)	24(1)	30(1)	31(1)	0(1)	-2(1)	-5(1)
Si(4)	29(1)	30(1)	29(1)	-5(1)	1(1)	-1(1)
Si(5)	30(1)	40(1)	22(1)	-1(1)	3(1)	-10(1)
Si(6)	26(1)	34(1)	23(1)	0(1)	0(1)	-11(1)
Si(7)	31(1)	30(1)	29(1)	2(1)	-1(1)	5(1)
Si(8)	40(1)	47(1)	30(1)	2(1)	2(1)	11(1)
C(1)	37(1)	24(1)	23(1)	2(1)	-1(1)	2(1)
C(2)	50(2)	62(2)	34(1)	-8(1)	6(1)	-6(1)
C(3)	68(2)	81(2)	35(1)	-16(1)	10(1)	8(2)
C(4)	81(2)	50(2)	30(1)	-10(1)	-10(1)	17(1)
C(5)	60(2)	50(2)	42(1)	-10(1)	-16(1)	-1(1)
C(6)	44(1)	47(1)	37(1)	-7(1)	-2(1)	-3(1)
C(7)	41(1)	38(1)	53(2)	1(1)	-5(1)	13(1)
C(8)	30(1)	67(2)	43(1)	5(1)	10(1)	-4(1)
C(9)	38(1)	58(2)	42(1)	-1(1)	-14(1)	-3(1)
C(10)	47(2)	44(1)	55(2)	3(1)	3(1)	-19(1)
C(11)	55(2)	50(2)	40(1)	-18(1)	1(1)	0(1)
C(12)	65(2)	46(1)	39(1)	13(1)	-17(1)	-16(1)
C(13)	49(2)	87(2)	42(2)	-16(1)	23(1)	-19(2)
C(14)	64(2)	33(1)	40(1)	0(1)	5(1)	-16(1)
C(15)	29(1)	77(2)	39(1)	0(1)	-1(1)	-16(1)
C(16)	46(2)	65(2)	40(1)	-1(1)	-16(1)	16(1)
C(17)	69(2)	38(1)	50(2)	14(1)	15(1)	-1(1)
C(18)	90(2)	42(2)	51(2)	2(1)	1(2)	14(2)
C(19)	47(2)	111(3)	43(2)	0(2)	7(1)	32(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1-phenylbicyclo[2.2.2]octasilane (**1**).

	x	y	z	U(eq)
H(2)	9846	1453	3695	58
H(3)	9776	648	2665	73
H(4)	7823	-45	2329	65
H(5)	5941	66	3031	61
H(6)	6008	872	4064	51
H(7A)	10196	745	5992	66
H(7B)	11725	992	5864	66
H(7C)	10837	582	5226	66
H(8A)	11228	2909	4477	70
H(8B)	11516	1989	4243	70
H(8C)	12397	2399	4883	70
H(9A)	11152	1984	7213	69
H(9B)	11556	2895	7438	69
H(9C)	12395	2421	6849	69
H(10A)	10496	4137	5608	73
H(10B)	11972	3803	5810	73
H(10C)	11144	4284	6399	73
H(11A)	8624	4270	7506	72
H(11B)	8744	3435	7950	72
H(11C)	7295	3810	7746	72
H(12A)	9205	1105	7151	76
H(12B)	7943	632	7461	76
H(12C)	8558	1405	7883	76
H(13A)	4953	2307	7125	89
H(13B)	5800	2183	7866	89
H(13C)	5189	1410	7443	89
H(14A)	7967	47	5879	68
H(14B)	6748	-93	5307	68
H(14C)	6477	-90	6151	68
H(15A)	4679	2051	5510	72
H(15B)	4326	1217	5908	72
H(15C)	4599	1217	5064	72
H(16A)	4864	2864	4443	76
H(16B)	5596	2887	3689	76
H(16C)	5172	3719	4070	76
H(17A)	9242	3823	4299	78
H(17B)	7994	4339	3978	78
H(17C)	8421	3508	3596	78
H(18A)	8619	4926	5633	91
H(18B)	7535	5221	6194	91
H(18C)	7176	5243	5347	91
H(19A)	4735	3431	6009	100
H(19B)	4680	4281	5586	100
H(19C)	5041	4264	6433	100

Table S6. Torsion angles [°] for 1-phenylbicyclo[2.2.2]octasilane (**1**).

Si(2)-Si(1)-C(1)-C(2)	-24.5(2)
Si(6)-Si(1)-C(1)-C(2)	-144.58(18)
Si(7)-Si(1)-C(1)-C(2)	96.87(19)
Si(1)-Si(2)-Si(3)-Si(4)	16.10(4)
Si(1)-Si(6)-Si(5)-Si(4)	21.15(4)
Si(1)-Si(7)-Si(8)-Si(4)	13.73(5)

2. Fluorescence Spectra of Phenyl[tris(trimethylsilyl)]silane (4) in Various Solvents

Phenyl[tris(trimethylsilyl)]silane (**4**) shows no ICT fluorescence in non-polar hexane as described in text; **4** shows only a weak LE fluorescence at 290 nm. Compound **4** however shows a very week ICT fluorescence band at 340 and 360 nm in polar CH_2Cl_2 and CH_3CN solvents, respectively, together with the LE fluorescence (Figure S3). The weak ICT fluorescence of **4** in polar solvents is in accord with the existence of a mechanism to stabilize the ICT state in polar solvents different from the OICT mechanism, as shown in our previous papers.[*1]

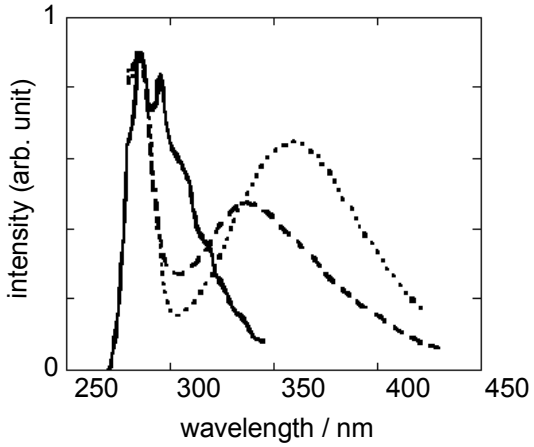

Figure S3. Fluorescence spectra of phenyltris(trimethylsilyl)silane (**4**); (a) in hexane (solid line); (b) in dichloromethane (dashed line); (c) in acetonitrile (right, dotted line).

*1. (a) H. Sakurai, H. Sugiyama and M. Kira, *J. Phys. Chem.*, 1990, **94**, 1837. (b) M. Kira, T. Miyazawa, H. Sugiyama, M. Yamaguchi and H. Sakurai, *J. Am. Chem. Soc*., 1993, **115**, 3116.